

PATENT SPECIFICATION

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 A257 A25X A25Y A280 A28X A28Y A307 A309
 A30Y A311 A313 A316 A319 A31X A320 A323
 A326 A329 A337 A339 A33Y A340 A341 A343
 A345 A347 A349 A350 A352 A354 A356 A358
 A35X A35Y A360 A362 A364 A366 A369 A36Y
 A377 A379 A37Y A381 A383 A385 A387 A389
 A38X A409 A41Y A422 A425 A428 A432 A435
 A437 A439 A43X A447 A449 A44Y A451 A453
 A455 A457 A459 A45X A48Y A503 A505 A507
 A509 A51Y A529 A533 A535 A537 A539 A53Y
 A541 A543 A545 A547 A549 A54X A579 A584
 A587 A589 A58Y A591 A593 A595 A599 A59X
 A609 A60Y A615 A617 A619 A61Y A621 A623
 A62X A671 A673 A674 A675 A677 A679 A67X
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(54) ALLOY

(71) We, CABOT CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 125 High Street, Boston, State of Massachusetts 02110, United States of America, (assignee of Robert Blanchard Herman Herchenroeder), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to nickel base alloys, and more particularly to a system of solid solution type nickel base alloys of the Ni-Cr-Fe class which are unusually stable and versatile by virtue of a combination of oxidation resistance and resistance to development of cracks in the heat affected zones produced during welding. The alloys provided are, therefore, particularly suited for use in structural parts designed for exposure to high-temperature oxidizing atmospheres, such as those commonly encountered in gas turbine engines.

U.S. Patent 3,304,176 to Wlodek shows that the addition of minor amounts of lanthanum is generally more beneficial in solid solution type nickel base alloys than in "pre-

cipitation strengthened" types. However, said patent does not teach the close control on the amount of lanthanum which is necessary for optimum weldability nor the essentiality of silicon and the optimum range of same to be used with lanthanum in this connection.

By practice of the present invention there may be provided both weldability and high temperature oxidation resistance of solution strengthened nickel base alloys. The present invention may also result in a range of alloys which are stable and versatile but not unduly expensive.

According to the present invention, there is provided a nickel base alloy having a combination of good weldability and high temperature oxidation resistance consisting, apart from impurities and minor amounts of incidental elements, in weight percent 15—29, and preferably 18—25%, chromium; 12—35%, and preferably 15—33%, iron; 38—72%, and preferably 40—60% or 40—70%, nickel and cobalt (taken together); between 0.2 and 2.5%, and preferably between 0.3 and 2% by weight silicon and lanthanum in small but effective amounts below 0.2%, and preferably between 0.02 and 0.12% by weight.

The preceding paragraph outlines the essential elements inherent in the alloys of this

invention with cobalt, although usually a subordinate or connate partner of the nickel, being acceptable for separate addition in amounts at least equal to nickel itself. Of course, other elements, though optional, are commonly incorporated in minor amounts for specific purposes in addition to various adventitious components. For example, fractional percentages of carbon are commonly added especially for castings. Likewise, small amounts of molybdenum and tungsten are generally included since they can contribute to solution strengthening or carbide dispersion strengthening. Accordingly, the minor optional ingredients of interest in this invention are (with amounts expressed in weight %): 0-1%, and preferably 0.02 to 0.2%, carbon; 0-5%, and preferably 1-4%, each of tungsten and molybdenum; and 0-3%, and preferably 0.5-2%, manganese.

Although various other common alloying ingredients such as zirconium, titanium, columbium or hafnium can be tolerated in small amounts in the present invention, they are merely incidental hereto and will generally be restricted to connate or adventitious amounts e.g. 1 or 2% by weight of the alloy. Traces or fractional percentages of other elements such as boron, nitrogen or aluminum are sometimes added for extraneous reasons as is known in the metallurgical arts, but again, these play no significant role in the present invention. For example, aluminum, magnesium or other deoxidants are sometimes added during the preparation of a melt, but usually only traces or fractional percentages are retained as a residual part of the finished alloy.

Any of the standard methods conventionally used in manufacturing superalloys can be used in preparing the alloys of this invention, e.g. air induction melting or vacuum melting. Other than the normal care required in analyzing constituents, intermediate combinations and finished melts to ensure attainment of the desired composition, the most critical step in the process is the addition of the lanthanum. In spite of the small amounts of lanthanum required in the present invention, the desired benefits therefrom can be obtained even if it is added in crude mixtures with other rare earth metals. However, cerium in particular appears to cause welding defects and it is, of course, the most prevalent constituent in mischmetal and other common rare earth ores. Accordingly, concentrated forms of lanthanum are preferably used in the present invention so that the lanthanum concentration at least exceeds the total of all the other rare earths. One of the most convenient forms for use in the present invention is that of a prealloy or master alloy of a refined lanthanum source with nickel, cobalt and/or silicon, since nickel and cobalt are base materials and silicon is required in amounts never less than the

maximum lanthanum content permitted. In any case, regardless of the form in which the lanthanum is added, it is normally convenient and efficient to add same to the alloy during the late stages of preparation thereof.

In the experimentation involved in the present invention, weldability was tested by measuring the hot cracking susceptibility in the heat-affected zone surrounding the actual fusion zone. The actual test method employed was one developed at the Welding Research Laboratory of Rensselaer Polytechnic Institute in Troy, New York, designed to use the augmented strain concept in measuring the hot cracking propensity of an alloy in sheet form. In the present work, the test sheets were 6 inches long by 1 inch wide and 1/16 inch thick. The specimen is held in a horizontal position in a jig. A gas shielded tungsten electrode arc torch is then used to form a puddle weld of suitable size at the center of the specimen on the upper side. After allowing time for the establishment of approximately steady state thermal conditions through the specimen around the puddle of molten metal, the desired augmented strain is introduced by loading the specimen at the center from below using a die block with a known symmetrical radius of curvature, mounted on a hydraulic ram. The movement of the ram is adjusted so that the mid-portion of the specimen sheet just conforms to the radius of the die block. The amount of augmented strain introduced is a function of the thickness of the sheet and the radius of curvature of the die block. In the present work, the radius of curvature was 4 inches so that the augmented strain introduced was about 0.9%.

A better understanding of the practice of this invention and the advantages that stem therefrom will be provided by the following experimental comparisons of specific alloy formulations exemplary of the invention with others of similar character but which are lacking in the critical parameters such as silicon and/or lanthanum content.

EXAMPLES 1 to 3.

Example I.

Using an air induction melting technique, several 20-pound ingots were made of a nickel base alloy consisting of 23.6% chromium, 16.4% iron, 0.05% carbon, 3.4% tungsten, 3.0% molybdenum, 3.7% cobalt, 0.55% manganese, 2.0% silicon and 0.1% aluminum, with the balance being nickel and adventitious impurities. Just prior to the casting of each of these ingots, small amounts of a relatively pure form of lanthanum were added so as to provide a series of ingots containing gradually increasing amounts of lanthanum ranging from about 0.02 to about 0.2%.

The resulting ingots were hot forged by pressing to slabs about $\frac{3}{4}$ " thick by $3\frac{1}{2}$ " wide. Subsequently, these slabs were hot rolled to

1/16" thick sheet, which was annealed and pickled to provide a clean surface finish. Four specimens were cut from each sheet and subjected to the hot cracking weldability test described hereinbefore. The total length of the cracks in the heat-affected zone surrounding the stationary weld puddle was then measured for each specimen and the average results are plotted in the accompanying drawing hereof versus the lanthanum content of the various specimens. The resulting curve indicates that amounts of lanthanum over 0.16% lead to rapid deterioration in weldability and that the optimum range is below about 0.12% by weight. Moreover, the oxidation resistance of these specimens containing from about 0.02

to about 0.12% lanthanum was excellent when tested at both 2000° F. and 2100° F. by means of the same procedure described in the next Example.

Example II.

In another series of tests, a group of five different alloys having the compositions shown in TABLE I below the balance in each case being Ni were prepared by air induction melting in approximately 40-pound heats of each. In each case, one 20-pound ingot was cast directly and a second one after addition of a small amount of lanthanum to provide a lanthanum content within the preferred range, i.e. less than 0.12% by weight.

TABLE I — NICKEL BASE ALLOYS
(without lanthanum)

Alloy	Composition in weight per cent								
	Cr	Fe	C	W	Mo	Co	Mn	Si	Al
A	25.2	17.1	0.04	3.1	2.9	2.4	1.5	1.1	0.04
B	23.1	16.9	0.05	2.8	2.9	0.5	1.5	0.6	—
C	20.5	19.5	0.06	3.0	2.9	3.5	0.8	1.6	—
D	20.9	32.5	0.10	2.7	2.8	19.8	1.1	0.6	0.11
E	20.2	49.2	0.22	3.0	3.9	10.1	0.5	0.4	—

Portions of each of the resulting 10 ingots were saved for oxidation resistance tests in the as-cast condition while the remainder of each was forged at about 2150° F. to plate and subsequently hot rolled to sheet of not more than 1/4" thickness. Hot workability was good in each instance with no apparent difference in workability between ingots made with and without lanthanum additions.

The data reported in TABLE II represent the average depth of metal lost at the temperatures shown assuming uniform penetration from the entire original surface when specimens of the above alloys were tested for oxidation resistance. Furthermore, each value reported in TABLE II is an average of values calculated from at least three specimens in each case.

The procedure for these oxidation resistance tests was as follows:

(1) Prepare specimens about 3/4" x 3/4" in size and having a thickness of between 0.03 and 0.25".

(2) Grind all surfaces to a 120 grit finish and degrease in acetone.

(3) Measure exact surface area and weight of each specimen.

(4) Expose specimens to dry air flow of more than 2 cu.ft./hr. through the furnace while maintaining a constant temperature therein for four 25-hour periods with the specimens being air cooled to room temperature after each 25-hour period.

(5) Reweigh each specimen.

(6) Descale specimens in salt bath.

(7) Carefully weigh the descaled specimens and calculate the weight loss of each.

(8) Convert these weight loss figures to "average depth of metal lost" values in accordance with the following formula:

$$\frac{\text{Measured Weight Loss}}{\text{Density of Alloy}} \times \frac{1}{\text{Surface Area of Specimen}}$$

TABLE II
OXIDATION TEST RESULTS

Alloy	Average Depth of Metal Lost, in mils		
	at 2000°F. As Cast	Wrought	at 2100°F. (Wrought only)
A	0.67	0.68	—
A + 0.06% La	0.25	0.22	0.27
B	0.67	0.55	—
B + 0.08% La	0.22	0.18	0.23
C	0.47	0.47	—
C + 0.08% La	0.18	0.19	0.22
D	1.11	1.03	—
D + 0.05% La	0.26	0.24	1.00
E	completely destroyed		—
E + 0.05% La	completely destroyed		—

The above results show that the controlled additions of lanthanum in the range of between about 0.05 and 0.08% (i.e. in the heart of the region in which weldability is optimized) very significantly upgraded the oxidation resistance of each of the above alloys except for alloy E. The complete failure of this alloy with or without the lanthanum addition shows the disastrous results of allowing the content of nickel and cobalt combined to fall significantly below 38% by weight. In this connection, it might be noted that alloy D which is

near but slightly above said lower limit of 38% on nickel and cobalt is still greatly improved by the lanthanum addition, as shown particularly in the 2000° F. test of oxidation resistance.

EXAMPLE III.

Two alloys relatively low in silicon content and having the compositions shown in TABLE III were made and tested using the preparation techniques and the weldability and oxidation resistance measurement methods of Examples I and II.

TABLE III
LOW SILICON, NICKEL BASE ALLOYS

Alloy:	Composition in per cent by weight									
	Cr	Fe	C	W	Mo	Co	Mn	Si	Al	La
F	15.5	34.2	0.15	0.8	1.2	—	0.3	0.05	0.22	0.16
G	15.2	34.0	0.14	0.8	1.2	—	0.3	0.31	0.19	0.18

Both of the above alloys, F and G, showed about the same propensity for developing cracks in the heat-affected zone during the augmented strain weldability test as described in Example I and both were borderline high in this regard because their lanthanum contents are higher than the optimum range for the

purposes of the present invention. However, most significantly, even at this relatively high level of lanthanum addition, the oxidation test results obtained as described in Example II reveal that the average depth of metal lost value for alloy G was only one fourth as great as that for alloy F even at 2100° F. This shows

the critical need for at least a moderate minimum content of silicon and accounts for the requirement of a minimum level of 0.2% silicon in the alloys of this invention. Although the silicon content can be as high as 2.5% maximum, the range between 0.3 and 2.0% is considered optimum and is preferred. The average depth of metal lost value for alloy G at 2100° F. was only 0.5 mils, which also demonstrates that reasonable oxidation resistance can be obtained by the present invention even at relatively low chromium contents of about 15%. Naturally, somewhat higher concentrations of chromium are preferred for optimum oxidation resistance, e.g. 18—25%. Tensile properties were also measured on alloys F and G at both room temperature and at 1600° F. These data are reported in TABLE IV.

TABLE IV
TENSILE DATA

Alloy	Test Temp. (°F.)	0.2% Offset Yield Strength (Ksi)	Ultimate Tensile Strength (Ksi)	Elongation (%)
F	70	46.6	95.8	42.5
F	1600	25.2	36.2	46
G	70	40.9	97.0	47
G	1600	24.9	36.2	44

The above results indicate that even at the higher levels of lanthanum addition (around 0.16 to 0.20%), the tensile properties are still excellent and that these are not affected significantly by the use of silicon in the amounts claimed herein.

Although specific embodiments of the present invention have been described in connection with the above illustrative Examples in order to show the separate effects of changes in content of certain key ingredients of the present alloys, it should be understood that various other modifications can be made by those having ordinary skills in the metallurgical arts without departing from the spirit of the invention taught herein. Therefore, the scope of this invention should be measured solely by the appended claims.

WHAT WE CLAIM IS:—

1. A nickel base alloy having a combination of good weldability and high temperature oxidation resistance consisting, apart from impurities and minor amounts of incidental elements, in weight per cent of:

Chromium	15 —29%
Iron	12 —35%
Nickel and Cobalt	38 —72%
Silicon	0.2— 2.5%
and Lanthanum in effective amounts	< 0.2%

2. An alloy as claimed in claim 1, in which the silicon content is from 0.3 to 2% by weight.

3. An alloy as claimed in claim 1 or 2, in which, the lanthanum content is from 0.02 to 0.12% by weight.

4. An alloy as claimed in any one of the preceding claims, in which the chromium content is from 18 to 25% by weight.

5. An alloy as claimed in any one of the preceding claims, in which the iron content is from 15 to 33% by weight.

6. An alloy as claimed in any one of the preceding claims in which the nickel and cobalt content taken together is from 40 to 70% by weight.

7. An alloy as claimed in any one of the preceding claims, which also contains carbon up to 1 per cent by weight.

8. An alloy as claimed in claim 7, in which the carbon content is from 0.02 to 0.2% by weight.

9. An alloy as claimed in any one of the preceding claims, which also contains tungsten up to 5% by weight.

10. An alloy as claimed in claim 9, in which, the tungsten content is from 1% to 4% by weight.

11. An alloy as claimed in any one of the preceding claims, which also contains molybdenum up to 5% by weight.

12. An alloy as claimed in claim 11, in which, the molybdenum content is from 1 to 4% by weight.

13. An alloy as claimed in any one of the preceding claims, which also contains manganese up to 3% by weight.

14. An alloy as claimed in claim 13, in which, the manganese content is from 0.5 to 2% by weight.

15. An oxidation resistant nickel base alloy having good weldability characteristics and consisting, apart from impurities and minor amounts of incidental elements, by weight of:

	Chromium	18	—25%	and with the balance being primarily nickel	
	Iron	15	—33%	and cobalt together with incidental additives	
	Nickel and Cobalt (plus			and adventitious elements, provided that the	
	incidental impurities)	40	—60%	total amount of rare earth elements other than	25
5	Tungsten	1	—5%	lanthanum is minimized and maintained be-	
	Molybdenum	1	—5%	low the lanthanum content.	
	Carbon	0.02—	0.2%	18. An alloy as claimed in claim 17, which	
	Silicon	0.3	—2%	also contains up to 3% manganese.	
	and Lanthanum in effective amounts	<0.12%		19. A nickel base alloy as claimed in claim	30
10	16. An alloy as claimed in claim 15 which			1 and substantially as hereinbefore described	
	also contains 0.5—2% manganese.			with reference to and as illustrated in the	
	17. An oxidation resistant nickel base alloy			accompanying drawing.	
	of excellent weldability comprising in weight			20. A nickel base alloy as claimed in claim	35
	per cent of:			1 and substantially as hereinbefore described	
				with reference to and as illustrated in any	
				one of the Examples.	
15	Chromium	15	—29%		
	Iron	12	—35%		
	Tungsten	1	—5%		
	Molybdenum	1	—5%		
	Carbon	0.02—	1.0%		
20	Silicon	0.2	—2%		
	and Lanthanum in effective amounts	<0.12%			

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EFFECT OF LANTHANUM
ON HOT CRACKING DURING WELDING

